SMITHSONIAN ~~INSTITUTION~~
ASTROPHYSICAL OBSERVATORY, Cambridge, Mass.

21 p.

SAO-SPECIAL REPT.-128)

Research in Space Science

SPECIAL REPORT

Number 128

Note: Initial cap. Special Rept. in body

ULTRAVIOLET SYNTHESIS OF ADENOSINE TRIPHOSPHATE UNDER POSSIBLE PRIMITIVE EARTH CONDITIONS

by

Cyril Ponnamperuma, Carl Sagan, and Ruth Mariner

July 10, 1963 21 pp refs

CAMBRIDGE 38, MASSACHUSETTS

SAO Special Report No. 128

ULTRAVIOLET SYNTHESIS OF ADENOSINE TRIPHOSPHATE UNDER POSSIBLE PRIMITIVE EARTH CONDITIONS

by

Cyril Ponnamperuma, Carl Sagan, and Ruth Mariner

(NASA Ames Res. Center)

Smithsonian Institution
Astrophysical Observatory
Cambridge 38, Massachusetts

ULTRAVIOLET SYNTHESIS OF ADENOSINE TRIPHOSPHATE UNDER POSSIBLE PRIMITIVE EARTH CONDITIONS

Cyril Ponnamperuma[1,2], Carl Sagan[3], and Ruth Mariner[1]

Introduction

It has been suggested that the prebiological synthesis of nucleoside phosphates on the primitive earth was a consequence of the absorption of ultraviolet light by purines and pyrimidines in an appropriate aqueous medium (Sagan, 1957, 1961b). The basis for this suggestion is as follows:

Even the simplest living organisms are statistically unlikely aggregations of organic molecules. The improbability of contemporary organisms is extracted from the field of possibilities through natural selection. But before the advent of self-replicating systems, natural selection as we understand it today could have played no such role. The origin and subsequent replication of life must therefore have involved molecules preferentially produced in the primitive environment. Such a view is implicit in the early works of Haldane (1929) and Oparin (1938). While it is possible that the fundamental molecular basis of living systems has itself evolved, the simplest working hypothesis holds that the molecules that are fundamental now were fundamental at the time of the origin of life. The production of amino acids, purines, pyrimidines and pentose sugars under simulated primitive conditions during the past decade lends support to this hypothesis.

---

[1]Exobiology Division, NASA Ames Research Center, Moffett Field, California.

[2]Research associate, National Academy of Sciences-National Research Council.

[3]Department of Genetics, Stanford University School of Medicine, Palo Alto, California. Permanent address: Department of Astronomy, Harvard University, and Smithsonian Astrophysical Observatory, Cambridge, Massachusetts.

There are, however, still several molecular species whose involvement in the origin of life remains to be demonstrated. Chief among these are the nucleoside phosphates. Adenosine triphosphate (ATP) is the "universal" energy intermediary of contemporary terrestrial organisms, and one of the major products of plant photosynthesis. The need for its production in primitive times was first emphasized by Blum (1951, p. 168). Guanosine triphosphate has recently been implicated as the energy source for peptide linkage (see, e.g., Schweet, 1963). The deoxynucleoside triphosphates are the precursors for contemporary DNA biosynthesis (Kornberg, 1959). To the extent that the origin of DNA plays a fundamental role in the origin of life, the abiogenic synthesis of deoxynucleoside triphosphates seems indicated (Sagan, 1961b). Several fundamental coenzymes of intermediate metabolism and plant photosynthesis (CoA, DPN, TPN, FAD) are nucleoside phosphates. All these molecules contain purines or pyrimidines, which have strong ultraviolet absorption maxima near 2600 Å. The possibility then arises that the absorption of ultraviolet photons by purines and pyrimidines provided the bond energy for the synthesis of nucleoside phosphates in primitive times; and it is therefore of some interest to investigate the ultraviolet transparency of the early terrestrial atmosphere.

There is astronomical evidence (Kuiper, 1952; Urey, 1952) that the earth's atmosphere was reducing at the time life first arose. Laboratory experiments have shown that it is far easier to synthesize organic matter under reducing than under oxidizing conditions (Garrison et al., 1951; Miller, 1957; Abelson, 1956). The molecules O_2 and O_3 are thermodynamically unstable in an excess of hydrogen, and the principal sources of the ultraviolet opacity of the present terrestrial atmosphere cannot have then been present. The ultraviolet absorption that did exist arose from intermediate oxidation state molecules, principally aldehydes and ketones. In experiments in which electrical discharges were passed through simulated primitive atmospheres, the only aldehyde or ketone produced in high yield was formaldehyde (Sagan and Miller, 1960). Nevertheless, the production of some acetaldehyde (see, e.g., Oró, 1963) and acetone can be expected. Formaldehyde absorption extends longward of about 2900 Å. Acetaldehyde and acetone absorb throughout the 2400 to 2900 Å region. Ammonia, acetylene, and other molecules absorb shortward of 2400 Å. Therefore, the question of the transparency of the primitive terrestrial atmosphere near 2600 Å turns mainly on the unknown early abundance of CH_3 CHO and CH_3 $COCH_3$. Because of the relatively low acetaldehyde and acetone yields in simulation experiments, and because of possible independent biological indications of high ultraviolet fluxes in primitive times (Sagan, 1961b), it seems likely that the early reducing atmosphere was at least slightly transparent between 2400 and 2900 Å. From models of the evolution of the sun, and an integration of the Planck function, the ultraviolet flux of wavelength $2900 \text{ Å} \geq \lambda \geq 2400 \text{ Å}$ incident on the earth's atmosphere 4×10^9 years ago is computed to be about 7×10^{14} photons cm^{-2} sec^{-1} (Sagan, 1961a). Even with substantial atmospheric absorption, ultraviolet radiation in this window will greatly exceed other energy sources for organic synthesis (Miller and Urey, 1961).

The synthesis of purines and pyrimidines which absorb in this wavelength region has recently been accomplished in a variety of primitive earth simulation experiments. Adenine has been produced by thermal polymerization of 1.5 molar HCN in an aqueous ammonia solution (Oró and Kimball, 1961); by 5 Mev electron irradiation of methane, ammonia, water and hydrogen (Ponnamperuma, Lemmon, Mariner, and Calvin, 1963); and by ultraviolet irradiation of a 10^{-4} molar solution of HCN (Ponnamperuma and Mariner, 1963b). Guanine also appears to be formed in the last experiment. Another guanine synthesis occurs in the thermal copolymerization of amino acids (Ponnamperuma, Young, and Muñoz, 1963). Uracil has been produced by heating urea and malic acid (Fox and Harada, 1961).

The yields of purines and pyrimidines are sometimes quite high. In the electron-beam irradiation of primitive atmospheres by Ponnamperuma, Lemmon, Mariner, and Calvin (1963) autoradiography indicates that the product produced in highest yield is adenine. Thus it appears possible that ultraviolet light passing the 2400 to 2900 Å partial window in the primitive terrestrial atmosphere was strongly absorbed by purines and pyrimidines in the early oceans.

The production rates of organic molecules from reducing atmospheres suggest that the primitive oceans were about a 1 percent solution of organic matter (Urey, 1952; Sagan, 1961b). In addition to purines and pyrimidines the pentose sugars, ribose and 2-deoxyribose, can be expected to be present. The laboratory production of 2-deoxyribose has been achieved through the condensation of formaldehyde and acetaldehyde, or of acetaldehyde and glyceraldehyde in aqueous salt solutions (Oró and Cox, 1962). (Indeed, this is an example of a mechanism that keeps the atmospheric aldehyde concentration low.) Both ribose and 2-deoxyribose have been synthesized by either ultraviolet or gamma irradiation of dilute formaldehyde solutions (Ponnamperuma and Mariner, 1963a). Phosphates and other phosphorus compounds can be expected in the primitive oceans, even at very early times (Rubey, 1951).

It therefore seems of some interest to attempt synthesis of nucleoside phosphates by ultraviolet irradiation of dilute solutions of purine or pyrimidine bases, pentose sugars, and phosphorus compounds, both because of our expectation that such syntheses were easily performed in primitive times, and because ultraviolet irradiation of dilute solutions of adenine and ribose has already produced the nucleoside adenosine (Ponnamperuma, Mariner, and Sagan, 1963).

Materials and experimental techniques

Adenine-8-C^{14} of specific activity 23.4 μc/mg, adenosine-8-C^{14} of specific activity 7.2 μc/mg, and adenylic acid-8-C^{14} of specific activity 3.1 μc/mg were supplied by Schwarz Bioresearch, Orangeburg, New York. The nonradioactive AMP, ADP and ATP used as carriers were supplied by C. F. Boehringer, Mannheim, Germany. The adenosine tetraphosphate was a gift of Dr. John Moffatt of Syntex Ltd., Palo Alto, California.

The ethyl metaphosphate used in the experiment was prepared by dissolving 150 gm of phosphorus pentoxide in 300 ml of ethyl ether and refluxing the solution for several hours with chloroform (Schramm et al., 1962). The excess solvent was removed by evaporation under vacuum, leaving a syrupy residue of ethyl metaphosphate.

The method of irradiation and analysis has already been described (Ponnamperuma, Mariner and Sagan, 1963). Quantities of the labeled adenine, adenosine, and adenylic acid, varying from 1.5×10^{-6} to 1.5×10^{-5} mole in various experiments, were sealed in aqueous solution in vycor tubes with approximately stoichiometric quantities of ribose, phosphoric acid or polyphosphate ester, as outlined in Table 1. The final concentration of base, nucleoside and nucleotide in each solution did not exceed 10^{-3} mole per liter. The solutions were irradiated by four G. E. ultraviolet germicidal lamps, type 782H-10, which emit 95 percent of their light in the Hg resonance line at 2537 Å. The vycor glass of which the tubes were made transmitted 80 percent of the light at this wavelength. During a 1-hour irradiation, the sample absorbed a total of $\sim 10^{8}$ ergs. During the irradiation the ambient temperature of the samples was $40 \pm 2^{\circ}C$.

The reaction products were first analyzed by paper chromatography, autoradiography and ultraviolet absorption studies. An aliquot of the reaction products was spotted on a Whatman No. 4 paper and the chromatogram run in two solvents, butanol-propionic acid-water (Bassham and Calvin, 1957, p. 19) and isobutyric acid-ammonia (Krebs and Hems, 1953). The positions of the carriers adenosine, AMP, ADP, ATP and A4P were detected by shadowgrams (Ponnamperuma, 1962). Coincidence both in position and in shape between the carriers on the shadowgrams and the radioactivity on the autoradiograph was the chromatographic basis for the identifications. The formation of adenosine has already been reported (Ponnamperuma, Mariner, and Sagan, 1963). A further aliquot was chromatographed in two other solvent systems, trichloroacetic acid-acetone (Burroughs, Grylls, and Harrison, 1952) and butanol-formic acid-water (Bennet, 1953). Once again there was coincidence between the carrier as outlined in the shadowgram and the radioactivity on the film.

Separations effected using thin-layer chromatography and ion-exchange chromatography confirmed the results obtained from paper chromatography.

Results

The results of the investigation are summarized in Table 1 and in Figures 1 through 4. Four different categories of experiments were performed. In the first the starting material was adenine, in the second adenosine, in the third adenosine monophosphate, and in the fourth adenosine diphosphate. The conversion of adenine to adenosine, adenosine to adenosine monophosphate, adenosine monophosphate to adenosine diphosphate, and adenosine diphosphate to adenosine triphosphate has been established. Experiments using adenine as the starting material have produced adenosine, AMP, ADP, and ATP.

The previously reported experiment showed that adenosine is not produced in detectable amounts in the absence of a phosphorus compound (Ponnamperuma, Mariner, and Sagan, 1963). While adenosine is produced in the presence of both phosphoric acid and ethyl metaphosphate, the nucleoside phosphates were detected only with the use of ethyl metaphosphate. Phosphoric acid was chosen first in the attempt to synthesize the nucleoside phosphates. Ethyl-metaphosphate was selected as a possible reagent because of a recent report (Schramm et al., 1962) that it activates carbonyl, hydroxyl and amino groups in organic synthesis. Other phosphorus compounds may also be effective in this synthesis, but they have not yet been investigated.

The yields are given in Table 1 and are further discussed below.

Controls

Two general categories of control experiments were performed to assess two possible modes of biogenic contamination of the reaction products. To test the possibility that the relatively high temperatures (40 ● 2° C) attained by the vycor tubes during ultraviolet irradiation stimulated the metabolic activities of microorganisms in the reactants, we placed control tubes at these same temperatures for comparable periods, but without ultraviolet irradiation. In all other respects they were handled and analyzed similarly to the irradiated samples. In no case was any yield detected.

An alternative hypothetical source of contamination is the presence in the labeled reactants of microorganisms which, under ultraviolet irradiation, are photolyzed, introducing their metabolic products into the medium. To test this possibility, we introduced into vycor tubes that had been autoclaved for 45 minutes at 120° C reactants that had been passed through an autoclaved Seitz filter. These sterile samples were then irradiated with ultraviolet light and analyzed. No change in yield was observed. We conclude that the microbiological contribution to the observed yields was negligible.

Discussion

The abiogenic nonenzymatic production of nucleoside phosphates and related molecules under simulated primitive earth conditions is relevant to the problem of the origin of life. The expected availability of ATP in primitive times suggests that energy was then available in convenient form for endergonic synthetic reactions of large molecules. The question arises why adenosine triphosphate, rather than, for example, the triphosphates of guanosine, cytidine, uridine, or thymidine, were not produced in primitive times and utilized today as the primary biological energy currency. There are several possible responses. In primitive earth simulation experiments under reducing conditions with low H_2 content, adenine is produced in far greater yield than are other purines and pyrimidines (Oró and Kimball, 1961; Ponnamperuma, Lemmon, Mariner, and Calvin, 1963; Ponnamperuma and Mariner, 1963b). Secondly, no biological purine or pyrimidine has a larger absorption cross-section between 2400 and 2900 Å. Thirdly, adenine is among the most stable of such molecules under ultraviolet irradiation. Finally the ultraviolet excitation energy is readily transferred, especially by π electrons, along the conjugated double bonds of the molecule; the excited states are very long-lived, and thereby serve to provide bond energies for higher synthetic reactions. All but the first of these properties of adenine derive from the fact that it has the greatest resonance energy of all the biochemical purines and pyrimidines (Pullman and Pullman, 1960, p. 111; Pullman and Pullman, 1962). It thus appears that molecules ideally suited for the origin of life were preferentially produced in primitive times.

The yields achieved in these experiments, as shown in Table 1, are relatively quite high. In contrast, quite elaborate methods are ordinarily required for the laboratory synthesis of nucleoside phosphates (Baddiley, 1955). For the production of adenosine from adenine, ribose, and a phosphorus source, the quantum yield for a 1-hour irradiation is $\varphi \sim 10^{-5}$. For production of AMP, ADP, and ATP by the use of ethyl metaphosphate, the quantum yields are almost an order of magnitude greater.

It is not now known to what extent the experiments here reported accurately reproduce the environmental conditions in the primitive terrestrial oceans. It can be expected that ethyl metaphosphate was probably not the most abundant phosphorus source, but we do not know how well other, possibly more abundant, phosphate salts may efficiently substitute for ethyl metaphosphate. The irradiation period in these experiments was $\sim$ 1 hour. Continued irradiation, with no removal of products, must, by the second law of thermodynamics, ultimately result in lower overall quantum yields. The influence of inorganic anions on the course and rate of these reactions is largely unknown. Nevertheless, it is of some heuristic interest to compute the production rate of adenosine triphosphate in the primitive terrestrial oceans, were the conditions there similar to those in the present experiments.

The production rate of ATP in the primitive reducing atmosphere will then be

$$\frac{d\sigma}{dt} \sim \frac{Q\ \varphi\ \mu}{4N_A} \text{ gm cm}^{-2} \text{ sec}^{-1} ,$$

where Q is the ultraviolet photon flux for 2400 Å $\leq \lambda \leq$ 2900 Å, φ is the quantum yield, μ is the molecular weight of ATP, and N_A is Avogadro's number (Sagan, 1961a). Taking $Q \sim 7 \times 10^{14}$ photons cm^{-2} sec^{-1} (Sagan, 1961a), $\varphi \sim 3 \times 10^{-5}$, and $\mu \sim 550$, we derive

$$\frac{d\sigma}{dt} \simeq 5 \times 10^{-12} \text{gm cm}^{-2} \text{ sec}^{-1} .$$

A feeling for the magnitude of this figure can be obtained by computing the steady-state population of microorganisms over the entire globe that could be maintained by this quantity of abiologically produced adenosine triphosphate. That is, we assume illustratively that the primitive earth is populated by obligate heterotrophs that obtain all their energy from abiologically synthesized ATP. We will obtain a minimum population if we assume that the number of ATP molecules required for each replication and the doubling time per cell have values characteristic of typical contemporary organisms. Taking values for Eschericia coli of 10^9 ATP molecules per cell for each doubling, and a doubling time of one hour, we find the required ATP production rate to maintain one cell must be 2.5×10^{-16} gm sec^{-1} cell^{-1}. The steady-state population of microorganisms that can be maintained over the entire globe by the abiological synthesis of ATP is then 2×10^4 cells per sq cm column of ocean. This estimate is of course extremely approximate. The assumptions that all the ultraviolet light is transmitted by the atmosphere, that it is all absorbed by adenine in the ocean, and that the quantum yields used in the ethyl metaphosphate experiments are applicable to the primitive environment probably increase the derived steady-state cell population; while the assumptions that the ATP requirement and doubling time for the primitive organisms are the same as for E. coli probably decrease the derived steady-state cell population over the true value. Nevertheless, this calculation does suggest that abiogenic ATP production by ultraviolet light in primitive times may have supported quite sizable populations of microorganisms on the primitive earth.

Such abiogenic production of ATP is, in effect, photosynthesis without life. One striking conclusion that has emerged from recent work on the mechanism of terrestrial plant photosynthesis is that the production of ATP is the primary, and most primitive, function of the photosynthetic apparatus (Arnon, 1961, p. 489; Calvin, 1962). The experimental results of the present paper permit us to understand why this might be so. With rather efficient abiogenic synthesis of so ideal an energy currency as ATP in the primitive environment, the transition from a reducing to an oxidizing atmosphere must have had profound results.

The transition was at least partially intitiated by the ultraviolet photodissociation of water vapor in the high atmosphere, and the selective escape of hydrogen to space (Kuiper, 1952; Urey, 1959). The ozone concentration of a planetary atmosphere depends approximately logarithmically on the oxygen concentration, down to a certain lower limit of the oxygen concentration (Marmo and Warneck, 1961; Paetzold, 1963); thus the steady-state production of even 10^{-4} or 10^{-5} of the present O_2 concentration would have produced enough ozone to diminish the ultraviolet flux in the 2400 to 2900 Å partial window, and make the rate of ultraviolet synthesis of ATP decline. A premium was then placed on organisms with the ability to utilize visible light for ATP synthesis. One can imagine the metabolism of the primitive organisms to be so keyed to the availability of ATP that the first visible photosynthetic apparatus evolved would be adopted by all subsequent life forms.

The precise mechanism of synthesis has not yet been investigated. Ultraviolet excitation of adenine accounts for the adenosine synthesis, but the participation of phosphorus compounds in the reaction is obscure. Synthesis of nucleoside phosphates must be more indirect, since it is difficult to imagine the excitation energy being transferred across the ribose molecule, which has no conjugated double bonds. Alternative possibilities, such as the production of activated adenine or ribose phosphates, remain to be investigated.

Further study of currently unidentified chromatographic features should both help clarify the mechanisms of synthesis, and cast light on other possible prebiological organic reactions. Ultraviolet irradiation of solutions of deoxyribose, purines or pyrimidines, and phosphate compounds may have some relevance for the problem of polynucleotide origins.

Bio-assay. To establish whether the ATP synthesized by us was biochemically active, a luminescence assay was performed using dehydrated firefly tails. The method described by Strehler and Trotter (1952) was used. (Firefly tails were supplied by Schwarz Bioresearch, Inc., Mount Vernon, New York.) The intensity of luminescence was measured by a Turner fluorometer. The decay curve of the luminescence was identical with that of an authentic sample of ATP. The concentration of ATP in the solution used, as determined by this method, corresponded within the limits of experimental error to the value obtained by spectrophotometric measurements.

Summary

Adenosine triphosphate is the principal energy currency in contemporary terrestrial organisms. It is of interest to investigate the possibility that ATP was produced in early times by prebiological organic syntheses. We have found that ATP and other nucleoside phosphates can be formed in high yield under simulated primitive earth conditions -- e.g., by ultraviolet irradiation of dilute aqueous solutions of adenine, ribose and ethyl metaphosphate.

Table 1

Experiment	Adenosine	AMP	ADP	ATP	A4P
1.					
(i) Adenine-C^{14} + Ribose	-				
(ii) Adenine-C^{14} + Ribose + Phosphoric Acid	+(0.01%)	-	-	-	-
(iii) Adenine-C^{14} + Ribose + Ethyl Metaphosphate	+(0.01%)	+(0.08%)	+(0.06%)	+(0.05%)	+(0.04%)
2.					
(i) Adenosine-C^{14} + Phosphoric Acid		-	-	-	-
(ii) Adenosine-C^{14} + Ethyl Metaphosphate		+(0.5%)	+(0.2%)	+(0.1%)	+
3.					
(i) Adenosine monophosphate-C^{14} + Phosphoric Acid			-	-	-
(ii) Adenosine monophosphate-C^{14} + Ethyl Metaphosphate			+(3%)	+(0.3%)	+(0.1%)
4.					
(i) Adenosine Diphosphate + Phosphoric Acid				-	-
(ii) Adenosine Diphosphate + Ethyl Metaphosphate				+	+

Figures within parentheses show conversion as percent of starting material.

With the techniques used in this experiment the lower limit of detectability was 0.001%

In experiment 4 no quantitative estimates were performed, as unlabeled ADP was used. The ATP in this case was located by shadowgrams.

Acknowledgement

One of us (C.S.) wishes to acknowledge stimulating conversations with Drs. Joshua Lederberg, Matthew Meselson and Jerome Schiff, and the partial support of his participation in this research by the National Aeronautics and Space Administration. We are grateful to Dr. John Moffatt for the gift of a sample of adenosine tetraphosphate.

References

ABELSON, P. H.
1956. Science, vol. 124, p. 935.

ARNON, D. I.
1961. In Light and Life. Eds., W. D. McElroy and B. Glass, The Johns Hopkins Press, Baltimore, p. 489.

BADDILEY, J.
1955. In The Nucleic Acids. Eds., E. Chargaff and J. N. Davidson, Academic Press, New York, Vol. 1, p. 137.

BASSHAM, J. A., and CALVIN, M.
1957. The Path of Carbon in Photosynthesis. Academic Press, New York, p. 19.

BENNET, E. L.
1953. Biochim. Biophys. Acta, vol. 12, p. 172.

BLUM, H. F.
1951. Time's Arrow and Evolution. Princeton University Press, Princeton, p. 168.

BURROUGHS, S., GRYLLS, F. S. M., and HARRISON, J. S.
1952. Nature, vol. 170, p. 800.

CALVIN, M.
1962. Perspectives in biology and medicine, vol. 5, p. 147.

FOX, S. W., and HARADA, K.
1961. Science, vol. 133, p. 1923.

GARRISON, W. M., MORRISON, D. C., HAMILTON, J. G., BENSON, A. A., and CALVIN, M.
1951. Science, vol. 114, p. 416.

HALDANE, J. B. S.
1929. Rationalist Annual, p. 148.

KORNBERG, A.
1959. Enzymatic synthesis of deoxyribonucleic acid. Harvey Lectures, Series 53, p. 83.

KREBS, H. A., and HEMS, R.
1953. Biochim. Biophys. Acta, vol. 12, p. 172.

KUIPER, G. P.
1952. In The Atmospheres of the Earth and Planets. Ed., G. P. Kuiper, University of Chicago Press, Chicago, 2nd edition, chapter 12, p. 304.

MARMO, F. F., and WARNECK, P.
1961. Geophysics Corporation of America Tech. Report 61-20-N.

MILLER, S. L.
1957. Biochim. Biophys. Acta, vol. 23, p. 480.

MILLER, S. L., and UREY, H. C.
1959. Science, vol. 130, p. 245.

OPARIN, A. I.
1938. The Origin of Life. Macmillan, New York.

ORÓ, J.
1963. Ann. N. Y. Acad. Sci. (in press).

ORÓ, J., and COX, A. C.
1962. Federation Proc., vol. 25, p. 80.

ORÓ, J., and KIMBALL, A. P.
1961. Arch. Biochem. Biophys., vol. 94, p. 217.

PAETZOLD, H.
1963. Proc. 11th International Astrophys. Colloq., Liège, p. 452.

PONNAMPERUMA, C.
1962. The radiation chemistry of nucleic acid constituents. University of California Radiation Laboratory Report 10053, p. 36.

PONNAMPERUMA, C., and MARINER, R.
1963a. Radiation Research, vol. 19, p. 183.

1963b. Paper to be presented at the 19th International Congress of Pure and Applied Chemistry, London, July.

PONNAMPERUMA, C., MARINER, R., and SAGAN, C.
1963. Nature, vol. 198, p. 1199.

PONNAMPERUMA, C., YOUNG, R. S., and MUÑOZ, E.
1963. Federation Proceedings (in press).

PONNAMPERUMA, C., LEMMON, R. M., MARINER, R., and CALVIN, M.
1963. Proc. Nat. Acad. Sci. U.S. (in press).

PULLMAN, B., and PULLMAN, A.
1960. Comparative Effects of Radiation. John Wiley and Sons, New York, p. 111.

PULLMAN, B., and PULLMAN, A.
1962. Nature, vol. 196, p. 1137.

RUBEY, W. W.
1951. Bull. Geolog. Soc. Amer., vol. 62, p. 1111.

SAGAN, C.
1957. Evolution, vol. 11, p. 40.

1961a. Organic matter and the moon. National Academy of Sciences-National Research Council Publication 757, 49 pp.

1961b. Radiation Research, vol. 15, p. 174.

SAGAN, C., and MILLER, S. L.
1960. Astron. Journ., vol. 65, p. 499.

SCHRAMM, G., et al.
1962. Angewandte Chemie, Int. ed., vol. 1, p. 1.

SCHWEET, R., and BISHOP, J.
1963. In Molecular Genetics. Ed., J. H. Taylor, Academic Press, New York, Chapter VIII.

SMITH, J. D., and MARKHAM, R.
1950. Biochim., vol. 46, p. 509.

STREHLER, B. L., and TROTTER, J. R.
1952. Arch. Biochem. Biophys., vol. 40, p. 28.

UREY, H. C.
1952. The Planets. Yale University Press, New Haven.

1959. In Handbuch der Physik. Ed., S. Flügge, Springer, Berlin, vol. 52, p. 363.

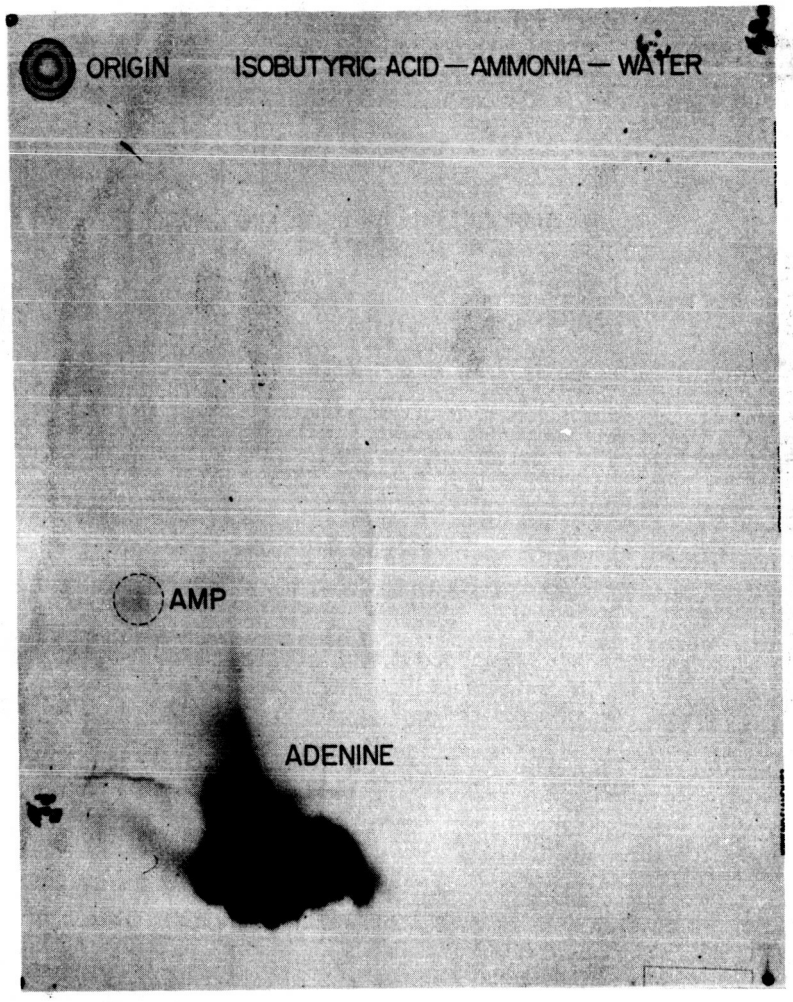

Figure 1.--Autoradiogram illustrating the formation of AMP from adenine, ribose and ethyl metaphosphate by the action of ultraviolet light.

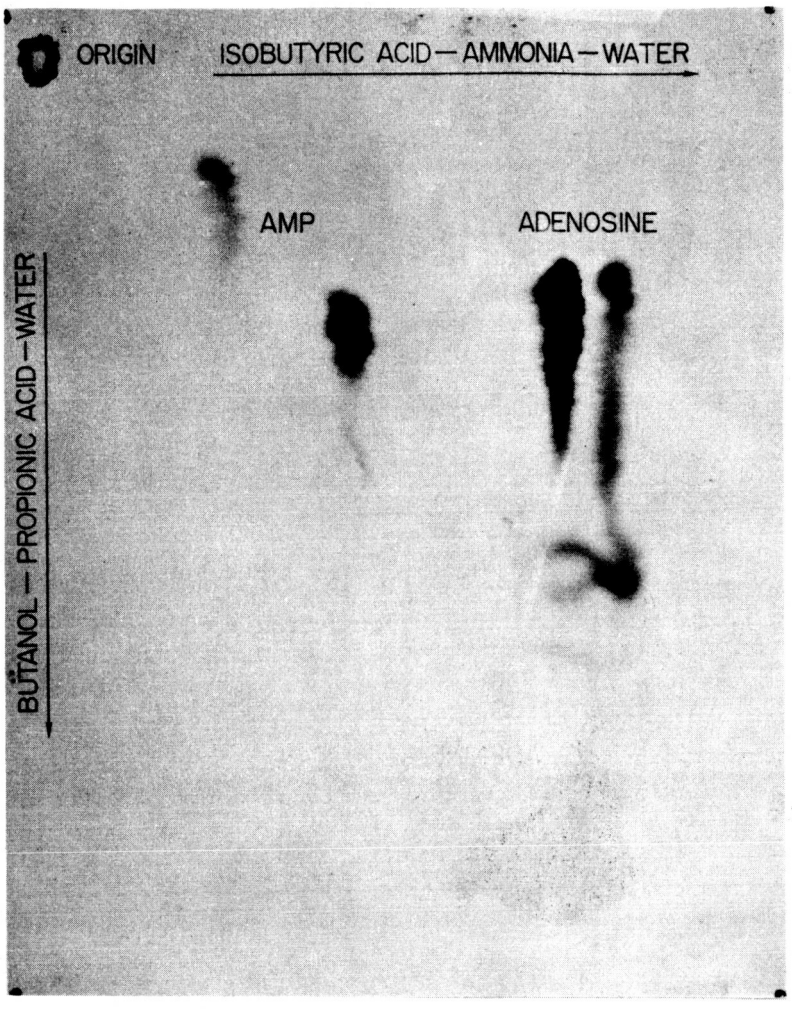

Figure 2.--Autoradiogram illustrating the formation of AMP from adenosine and ethyl metaphosphate by the action of ultraviolet light. The long feature to the right of the teardrop-shaped adenosine spot is adenine, produced from adenosine photolysis. The dark central feature between AMP and adenosine is at present unidentified.

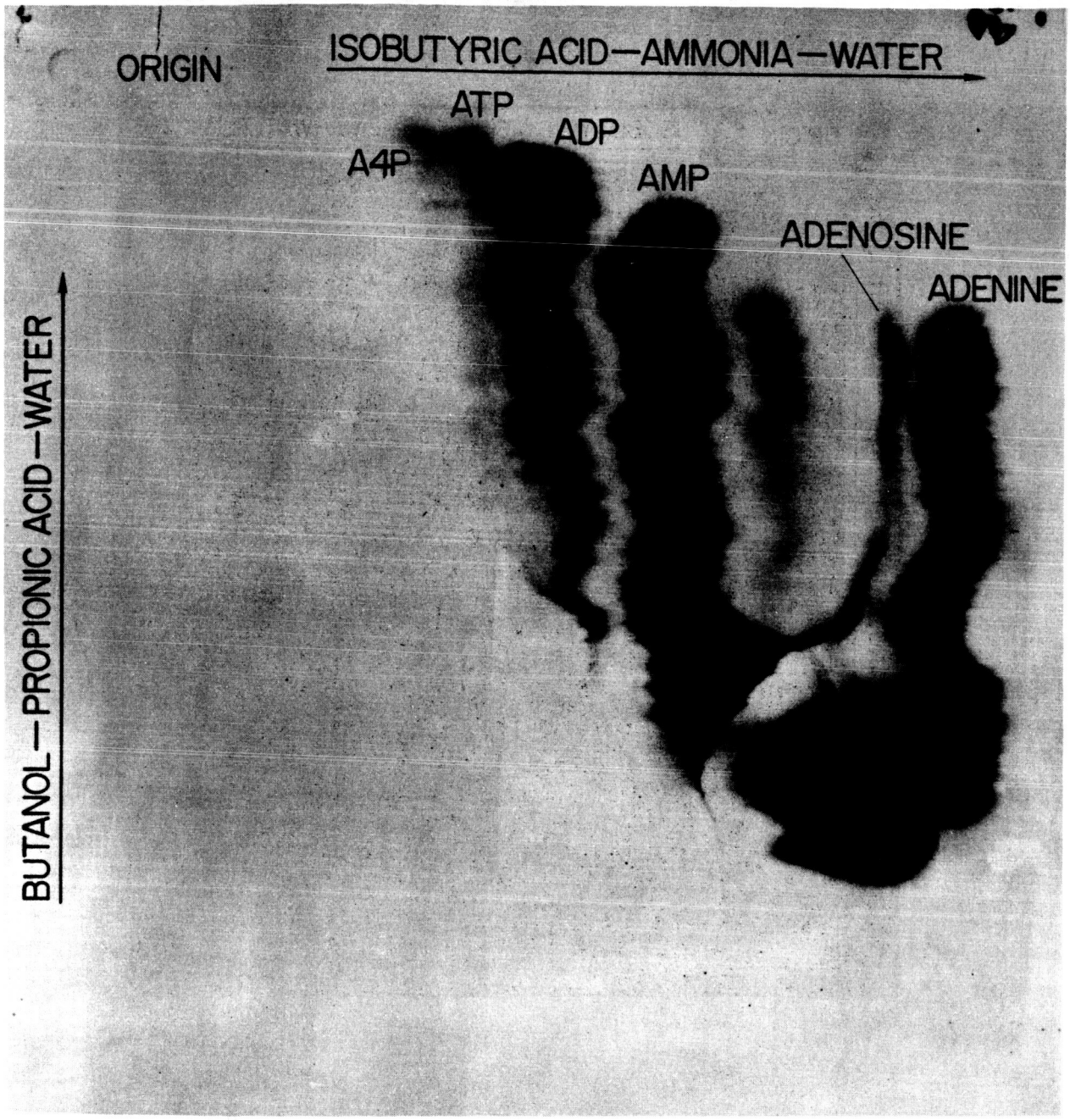

Figure 3.-- Autoradiogram illustrating formation of ADP, ATP and A4P from AMP and ethyl metaphosphate by the action of ultraviolet light.

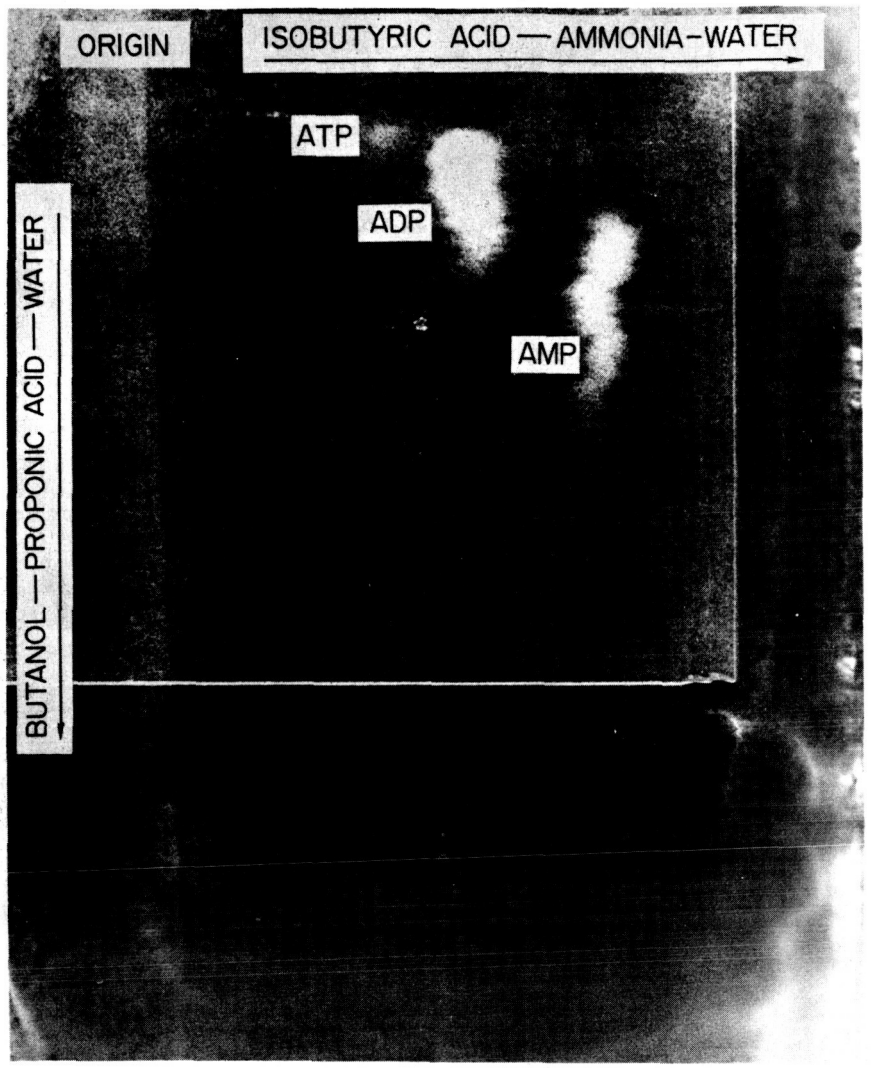

Figure 4.--Shadowgram illustrating the formation of ATP from ADP and ethyl metaphosphate by the action of ultraviolet light. The AMP is a photolytic product.

NOTICE

This series of Special Reports was instituted under the supervision of Dr. F. L. Whipple, Director of the Astrophysical Observatory of the Smithsonian Institution, shortly after the launching of the first artificial earth satellite on October 4, 1957. Contributions come from the Staff of the Observatory. First issued to ensure the immediate dissemination of data for satellite tracking, the Reports have continued to provide a rapid distribution of catalogues of satellite observations, orbital information, and preliminary results of data analyses prior to formal publication in the appropriate journals.

Edited and produced under the supervision of Mr. E. N. Hayes, the Reports are indexed by the Science and Technology Division of the Library of Congress, and are regularly distributed to all institutions participating in the U.S. space research program and to individual scientists who request them from the Administrative Officer, Technical Information, Smithsonian Astrophysical Observatory, Cambridge 38, Massachusetts.